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A PERTURBATION THEORY OF ISOELECTRONIC MOLECULES: CONVERGENCE OF SERIES FOR ONE DIMENSIONAL DELTA POTENTIAL MODEL

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ABSTRACT

The perturbation theory of heteronuclear molecules based on isoelectronic homonuclear molecules developed by Chang and Byers Brown is applied to the delta potential model. The radii of convergence of the series expansions for the energy and dipole moment are obtained. The errors in the perturbation treatment due to neglect of higher order terms are calculated. The results tend to support the application of this theory to the $CO-N_2$ problem.

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Introduction

The quantum mechanical problem for the heteronuclear diatomic molecule AB can be solved using a perturbation method with the isoelectronic homonuclear molecule as the unperturbed system. This theory is developed and applied to the isoelectronic molecules CO and N_2 by Chang and Byers Brown[1].

If Z_A, Z_B are the nuclear charges of A and B, respectively, then the Hamiltonian for the molecule AB can be written as $H = H_o + \lambda V$ where H_o is the Hamiltonian for the isoelectronic homonuclear molecule and

$$\lambda = (Z_A - Z_B)/(Z_A + Z_B)$$

is the perturbation parameter. The electronic energy can be formally written as

$$E = E_0 + E_2\lambda^2 + E_4\lambda^4 + \cdots, \qquad (1)$$

where all terms involving odd powers of λ vanish because of the symmetry of the unperturbed system. For the same reason, the series expansion for the dipole moment of the molecule AB contains only odd powers of λ, that is

$$\langle\mu\rangle = \mu_1\lambda + \mu_3\lambda^3 + \mu_5\lambda^5 + \cdots . \qquad (2)$$

In order to justify the treatment of CO based on N_2 mentioned above, it is necessary to know the radii of convergence of the series (1) and (2). Unfortunately, this is almost impossible for the CO-N_2 problem, which involves fourteen electrons. The object of this paper is to investigate the convergence of series (1) and (2) for the delta potential model introduced by Frost (2). This simplified problem can be solved exactly and it is hoped will reproduce the principle features of the actual molecular problem.

Delta function potential model for one-electron diatomic molecules

The model for a one-electron molecule AB consists of an electron moving along the X-axis with potential energy (atomic units)

$$U = -Z_A\delta(x+\tfrac{1}{2}R) - Z_B\delta(x-\tfrac{1}{2}R), \qquad (3)$$

where $\delta(x)$ is the Dirac delta function and R is the internuclear separation. The Hamiltonian for this model is therefore

$$H = -\tfrac{1}{2}\frac{d^2}{dx^2} - Z_A\delta(x+\tfrac{1}{2}R) - Z_B\delta(x-\tfrac{1}{2}R)\,. \qquad (4)$$

The Schrödinger equation can be solved exactly (Frost, 1956). Two bound state wave functions exist, of the form

$$\psi = a \exp(-\gamma|x+\tfrac{1}{2}R|) + b \exp(-\gamma|x-\tfrac{1}{2}R|), \quad (5)$$

where the two possible values for γ are roots of the equation

$$\gamma^2 - (Z_A+Z_B)\gamma + Z_A Z_B [1 - \exp(-2\gamma R)] = 0. \quad (6)$$

The energy eigenvalues are given by

$$E = -\tfrac{1}{2}\gamma^2. \quad (7)$$

The greater of the two solutions of equation (6) corresponds to the ground state and is given by

$$\gamma_g = \tfrac{1}{2}\left\{Z_A+Z_B + [(Z_A-Z_B)^2 + 4Z_A Z_B \exp(-2\gamma_g R)]^{\frac{1}{2}}\right\}. \quad (8)$$

If we introduce the variables

$$p = \gamma_g/Z_0, \quad s = Z_0 R \quad \text{where} \quad Z_0 = \tfrac{1}{2}(Z_A+Z_B),$$

then Eq. (7) and (8) can be put into the new forms

$$E = -\tfrac{1}{2} Z_0^2 p^2 , \tag{7'}$$

$$p = 1 + \exp(-sp)\sqrt{1 + \lambda^2 [\exp(sp) - 1]} \ . \tag{8'}$$

Perturbation expansion of energy

If we regard λ as a perturbation parameter then p may be expanded in even powers of λ for λ sufficiently small, that is

$$p = p_0 + p_2 \lambda^2 + p_4 \lambda^4 + \cdots \ . \tag{9}$$

The coefficients p_0 , p_2 , p_4 , etc. are determined by substituting Eq. (9) into Eq. (8'), expanding the term

$$\exp(-sp)\sqrt{1 + \lambda^2 [\exp(sp) - 1]}$$

in a power series in λ , and equating the coefficients of equal powers of λ on both sides of the equation. The results for the first three coefficients in Eq. (9) are

$$p_0 = 1 + \exp(-s p_0), \tag{10}$$

$$p_2 = \frac{p_0(2-p_0)}{2(p_0-1)(1-s+sp_0)}, \tag{11}$$

$$p_4 = \frac{4sp_2[1+(1+sp_2)(p_0-1)^2] - p_0^2(2-p_0)^2}{8(p_0-1)^3(1-s+sp_0)}. \tag{12}$$

From Eq. (7') we get the coefficients in the series expansion for energy, Eq. (1):

$$E_0 = -\tfrac{1}{2} z_0^2 p_0^2, \tag{13}$$

$$E_2 = -z_0^2 p_0 p_2, \tag{14}$$

$$E_4 = -\tfrac{1}{2} z_0^2 (p_2^2 + 2p_0 p_4). \tag{15}$$

For the case $s = 1$ and $z_0 = 1/2$ (neutral molecule) equations (10) - (15) give the following results

$p_o = 1.278465, \qquad p_2 = 1.295561, \qquad p_4 = -1.709585$

$E_o = -0.204309, \qquad E_2 = -0.414082, \qquad E_4 = 0.336601$

In Table 1, the expression $(E_2 + \lambda^2 E_4)$ is compared with the expression $(E-E_o)/\lambda^2$ for s = 1 and different values of λ. These quantities are also plotted in Figure 1 for in the range (0,1).

Radius of convergence of energy series

In order for the power series for p in equation (9) to be convergent, we must have

$$\lambda^2 [\exp(2sp) - 1] < 1. \tag{16}$$

From equations (8') and (16), the radius of convergence λ_c for the series (9), which is the same as that of the energy series, is given by

$$\lambda_c = [\exp(2sp) - 1]^{-\frac{1}{2}} = \frac{p_c - 1}{\sqrt{1 + 2p_c - p_c^2}}, \tag{17}$$

where p_c is the solution of the equation

$$p_c = 1 + \exp(-sp_c)\sqrt{2}. \tag{18}$$

The radius of convergence, λ_c , and the energy

$$E_c = -\tfrac{1}{2} z_0^2 p_c^2,$$

are displayed in Table 2 for a range of values of s .

Dipole moment calculation

The dipole moment with respect to the center of charge of the heteronuclear molecule AB is

$$\langle \mu \rangle = \langle \psi, \mu \psi \rangle / \langle \psi, \psi \rangle, \tag{19}$$

where ψ is given by equation (5) with

$$a/b = \exp(sp)\left(\frac{p}{1-\lambda} - 1\right), \tag{20}$$

and

$$\mu = -\left(x - \tfrac{1}{2}R + z_B R/2z_0\right). \tag{21}$$

The dipole moment has been defined to be positive for A^-B^+, and it is taken with respect to the center of charge of the system so that in the limit when the molecule dissociates into an atom and an ion ($\lambda \to 1$), $<\mu>$ goes to zero.

By substituting into (19) from equations (5), (20) and (21), we get

$$<\mu> = (s\lambda/2z_0)\left\{\left[(p-1)+s(p-1)^2-s\lambda^2\right]^{-1} - 1\right\}. \qquad (22)$$

The expansion of $<\mu>$ as a power series in λ is given by Eq. (2). The coefficients may be obtained by means of equations (9) and (22):

$$\mu_1 = (s/2z_0)\left\{\left[p_0 - 1 + s(p_0-1)^2\right]^{-1} - 1\right\},$$

$$\mu_3 = -\mu_1 \frac{\left[p_2 + 2s(p_0-1) - s\right]}{p_0 - 1 + s(p_0-1)^2},$$

$$\mu_5 = -\frac{\mu_3\left[p_2 + 2sp_2(p_0-1) - s\right] + \mu_1\left[p_4 + sp_2^2 + 2sp_4(p_0-1)\right]}{p_0 - 1 + s(p_0-1)^2}.$$

For $s = 1$, $Z_o = 0.5$, $\mu_1 = 1.808925$, $\mu_3 = -8.02496$, $\mu_5 = 30.6846$.

The exact values of $\langle\mu\rangle$ have been calculated from Eq. (22) for the case $Z_o = 0.5$, $s = 1$ and are listed in Table 3; the values of $\mu_1\lambda$, $(\mu_1\lambda + \mu_3\lambda^3)$ and $(\mu_1\lambda + \mu_3\lambda^3 + \mu_5\lambda^5)$ for the same values of Z_o and s are also given. These quantities are plotted in Figure 2.

We can also expand $\langle\mu\rangle$ in a power series in s if we have the series for p in powers of s. It follows from Eq. (8') that

$$p = 2 - 2(1-\lambda^2)s + 4(1-\lambda^2)s^2 + \cdots . \qquad (23)$$

The expansion of $\langle\mu\rangle$ in powers of s is therefore

$$\langle\mu\rangle = s^2\lambda(1-\lambda^2)/2z_0 - s^3\lambda(1-\lambda^2)[4z_0 - \lambda(1-\lambda^2)]/4z_0^2 + \cdots (24)$$

For the case $Z_o = 1/2$, $\lambda = 1/7 = 0.1428$, we get

$$\langle\mu\rangle = (0.139942)\, s^2 - (0.142798)\, s^3 + \cdots .$$

The exact values of $\langle\mu\rangle$ for various s and $Z_o = 0.5$,

λ = 0.142857 were obtained from Eq. (22) and are listed in Table 4. The plot of $\langle\mu\rangle$ against s is given in Figure 3.

Radius of convergence of dipole moment series

The series $(\mu_1\lambda + \mu_3\lambda^3 + \ldots\ldots)$ in Eq. (2) converges for all $\lambda \leq \lambda_c$ where $\lambda_c(s)$ is the radius of convergence of the power series expansion for p for any fixed value of s. This can be seen as follows. Equation (22) may be re-written in the form

$$\langle\mu\rangle = (s\lambda/2z_0)[p_0 - 1 + s(p_0-1)^2]^{-1}\left\{\frac{1}{1+f(\lambda)} - p_0 + 1 - s(p_0-1)^2\right\}, \quad (25)$$

where

$$f(\lambda) = \frac{p - p_0 + s(p-p_0)(p+p_0-2) - s\lambda^2}{p_0 - 1 + s(p_0-1)^2}, \quad (26)$$

and is of second order in λ.

In the case $f(\lambda) \geq 0$ it follows from equations (8') and (10), that $p \geq p_0$ for all $s \geq 0$ and λ in the range $(0,1)$. Also

$$p - p_0 + s(p-p_0)(p+p_0-2) = \exp(-sp)\sqrt{1+\lambda^2[\exp(2sp)-1]} - \exp(-sp_0)$$

$$+ s\left[\exp(-2sp)\{1+\lambda^2[\exp(2sp)-1]\} - \exp(-2sp_0)\right],$$

so that for $\lambda \leq \lambda_c$,

$$p - p_0 + s(p-p_0)(p+p_0-2) \leq \exp(-sp)\sqrt{2} - \exp(-sp_0)$$

$$+ s\left[2\exp(-2sp) - \exp(-2sp_0)\right]$$

$$< \exp(-sp_0) + s\exp(-2sp_0)$$

$$= p_0 - 1 + s(p_0-1)^2.$$

Hence for $f \geq 0$

$$f(\lambda) \leq \frac{p - p_0 + s(p-p_0)(p+p_0-2)}{p_0 - 1 + s(p_0-1)^2} \leq 1.$$

In the case $f(\lambda) < 0$, we have

$$f(\lambda) = \frac{(p-1) + s(p-1)^2 - s\lambda^2 - (p_0-1) - s(p_0-1)^2}{p_0 - 1 + s(p_0-1)^2}$$

$$= \frac{(p-1) + s(p-1)^2 - s\lambda^2}{p_0 - 1 + s(p_0-1)^2} - 1$$

$$\geq -1$$

since

$$(p-1) + s(p-1)^2 - s\lambda^2 = (p-1) + s(1-\lambda^2)\exp(-2sp) \geq 0.$$

In either case, the inequality $|f(\lambda)| \leq 1$ is always satisfied for all $\lambda \leq \lambda_c(s)$. The expansion of the function

$$(1+f(\lambda))^{-1}$$

in powers of λ is valid for all λ in this range. Therefore, the radius of convergence of the dipole moment series is greater than or equal to $\lambda_c(s)$ for all values of s.

Conclusion

It is interesting to attempt to use the results obtained in this paper to assess the application of the theory to CO based on N_2.

The neutral case has a Z_o value of 0.5, and if we use an R value of 2.0, which is about the equilibrium distance of CO and N_2, we get an s value of 1.0. From Table 2, we see that the radius of convergence in this case is 0.2649, which is greater than the λ value for the $CO-N_2$ problem which is $1/7 = 0.1428$.

From Table 1 we see that when $s = 1$, the leading term $\lambda^2 E_2$ differs from $(E - E_o)$ by less than 5.2 per cent for $\lambda \leq \lambda_c = 0.2649$. In Table 3 the term $\lambda\mu_1$

differs from the exact $\langle\mu\rangle$ value by less than 10.1 per cent for $\lambda \leq 0.15$. The results obtained from the model therefore support the $CO\text{-}N_2$ perturbation treatment.

References

1. Chang, Tai Yup and Byers Brown, W., University of Wisconsin Theoretical Chemistry Institute Report WIS-TCI-114 (August, 1965).

2. Frost, A. A., J. Chem. Physics, 22, 1150 (1956).

TABLE 1

Error in Energy E through Second and Fourth Orders divided by λ^2, for $s = 1$, $Z_0 = 1/2$

λ	$(E-E_0)/\lambda^2$	$(E-E_0-\lambda^2E_2)/\lambda^2$	$(E-E_0-\lambda^2E_2-\lambda^4E_4)/\lambda^2$
0	-0.414082	0	0
0.05	-0.413247	-0.000835	-0.000006
0.10	-0.410793	-0.004124	-0.000077
0.15	-0.406884	-0.007198	-0.000375
0.20	-0.401755	-0.012327	-0.001137
0.25	-0.395654	-0.018428	-0.002609
0.264932	-0.393688	-0.020394	-0.003231
0.30	-0.388864	-0.025218	-0.005076
0.35	-0.381619	-0.041233	-0.008770
0.40	-0.374121	-0.053856	-0.013895
0.45	-0.366533	-0.068162	-0.020613
0.50	-0.358978	-0.084888	-0.029046
0.55	-0.351547	-0.101822	-0.039287
0.60	-0.344305	-0.121176	-0.051399
0.65	-0.337294	-0.142214	-0.065425
0.70	-0.330537	-0.164934	-0.081489
0.75	-0.324051	-0.189338	-0.099307
0.80	-0.317842	-0.215425	-0.119184
0.85	-0.311907	-0.243194	-0.141019
0.90	-0.306243	-0.272647	-0.164808
0.95	-0.300841	-0.303782	-0.190541
1.00	-0.295691	-0.336601	-0.218210

Table 2

Radius of Convergence λ_c of energy as a function of Internuclear Separation $s = R\mathcal{Z}_0$

s	λ_c	$E_c/\mathcal{Z}_0^2$
0.10	1.367565	-2.293183
0.20	0.917867	-1.913551
0.30	0.710832	-1.655032
0.40	0.583663	-1.466849
0.50	0.494569	-1.323473
0.60	0.427567	-1.210542
0.70	0.374690	-1.119313
0.80	0.331568	-1.044133
0.90	0.295560	-0.981182
1.00	0.264932	-0.927770
1.20	0.215499	-0.842298
1.40	0.177267	-0.777308
1.60	0.146879	-0.726631
1.80	0.122266	-0.686366
2.00	0.102076	-0.653923
2.10	0.093328	-0.640049
2.20	0.085352	-0.627501
2.30	0.078071	-0.616133
2.40	0.071416	-0.605815
2.50	0.065327	-0.596440
3.00	0.041748	-0.560730
4.00	0.016670	-0.523850

Table 3

Dipole Moment as a Function of λ for $s = 1$, $z_0 = 1/2$

λ	$\langle\mu\rangle$	$\mu_1\lambda$	$\mu_1\lambda + \mu_3\lambda^3$	$\langle\mu\rangle - \mu_1\lambda$
0.01	0.018082	0.018090	0.018082	-0.000008
0.05	0.089452	0.090446	0.089444	-0.000994
0.10	0.173164	0.180892	0.172868	-0.007728
0.15	0.246388	0.271338	0.244254	-0.024950
0.20	0.306020	0.361786	0.297586	-0.055766
0.25	0.350710	0.452232	0.326842	-0.101522
0.264932	0.361122	0.479242	0.330016	-0.118120
0.30	0.380556	0.542678	0.326004	-0.162122
0.35	0.396656	0.633122	0.289054	-0.236466
0.40	0.400624	0.723571	0.209972	-0.322947
0.45	0.394244	0.814016	0.082748	-0.419772
0.50	0.379250	0.904462	-0.098658	-0.525212
0.55	0.357202	0.994908	-0.340244	-0.637706
0.60	0.329434	1.085354	-0.648036	-0.755920
0.65	0.297066	1.175800	-1.028050	-0.878734
0.70	0.261010	1.266248	-1.486314	-1.005238
0.75	0.222014	1.356694	-2.028836	-1.134680
0.80	0.180670	1.447140	-2.661638	-1.266480
0.85	0.137454	1.537586	-3.390742	-1.400132
0.90	0.092746	1.628032	-4.222164	-1.535286
0.95	0.046846	1.718478	-5.161922	-1.671632
1.00	0.000000	1.808926	-6.216036	-1.808926

TABLE 4

Dipole moment as a Function of Internuclear Separation $s = Rz_0$ for $\lambda = 1/7$, $z_0 = 1/2$

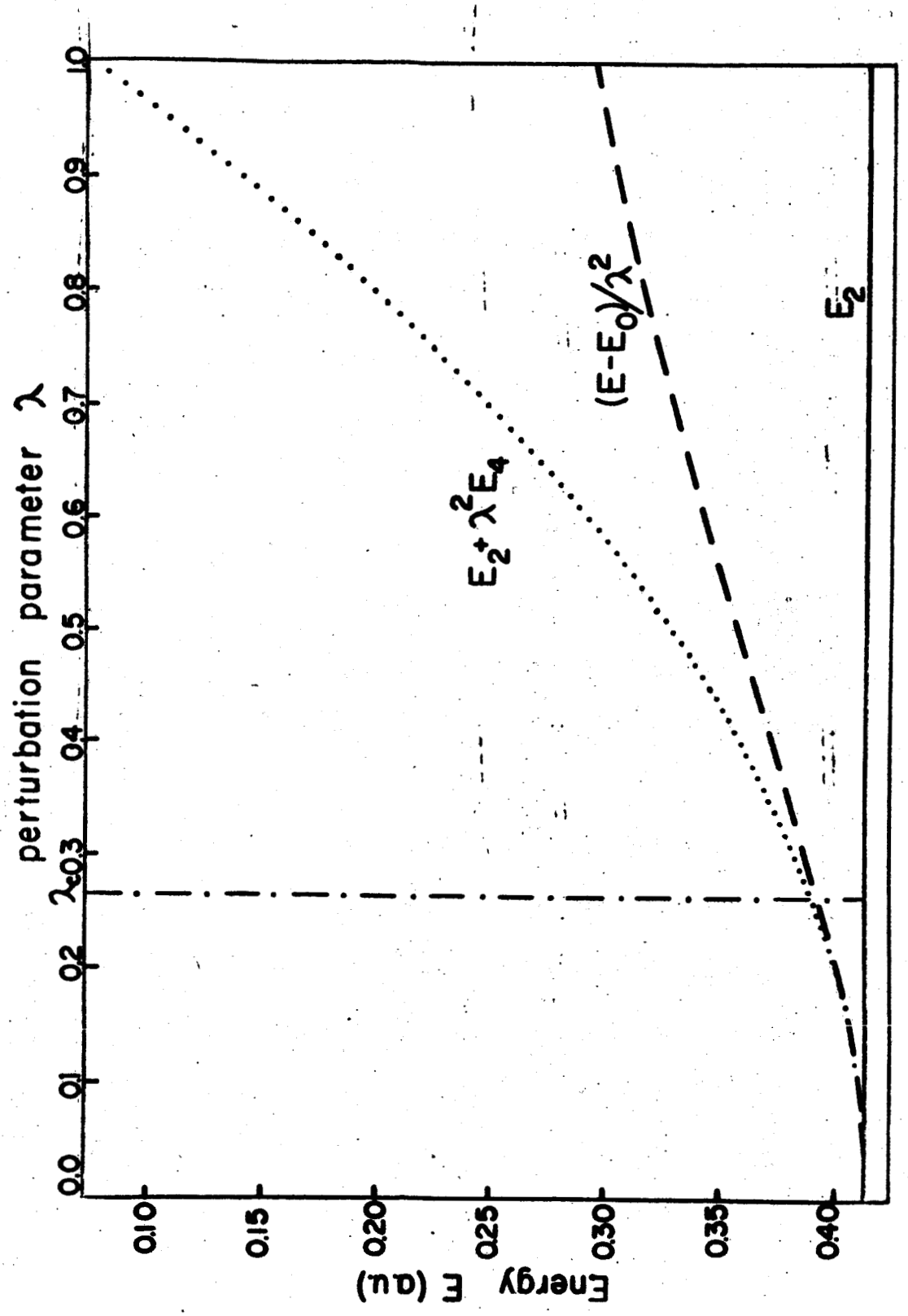
s	$\langle\mu\rangle$
0.01	0.000014
0.05	0.000366
0.10	0.001518
0.15	0.003534
0.20	0.006480
0.30	0.015420
0.40	0.028872
0.50	0.047384
0.60	0.071542
0.70	0.101944
0.80	0.139210
0.90	0.183940
1.00	0.236700
1.20	0.368132
1.50	0.632742
2.00	1.220874
2.50	1.862646
3.00	2.440782
3.50	2.945250
4.00	3.406904

Legends for Figures

Figure 1. Energy quantities (a.u.) as functions of λ for $s = 1$, $z_0 = \frac{1}{2}$: —— E_2 , ---- $(E-E_0)/\lambda^2$ .....$E_2 + \lambda^2 E_4$.

Figure 2. Dipole moment (a.u.) as function of λ for $s = 1$, $z_0 = \frac{1}{2}$: —— μ ; - - - - $\mu_1\lambda$, ... $\mu_1\lambda + \mu_3\lambda^3$.

Figure 3. Dipole moment (a.u.) as function of $s = Rz_0$ for $\lambda = 1/7$, $z_0 = \frac{1}{2}$.



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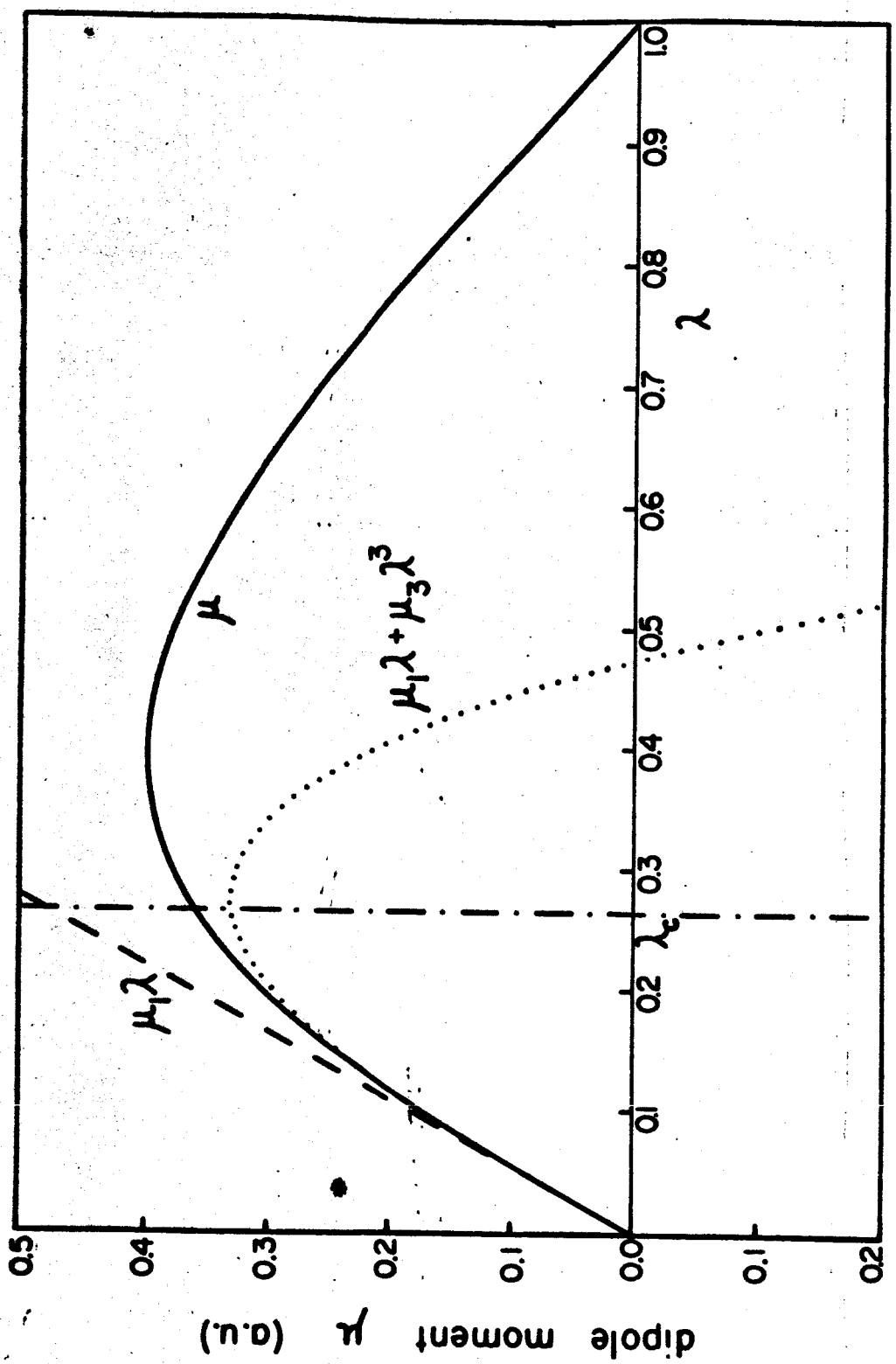

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—— μ ; ---- $\mu_1\lambda$, ... $\mu_1\lambda + \mu_3\lambda^3$.

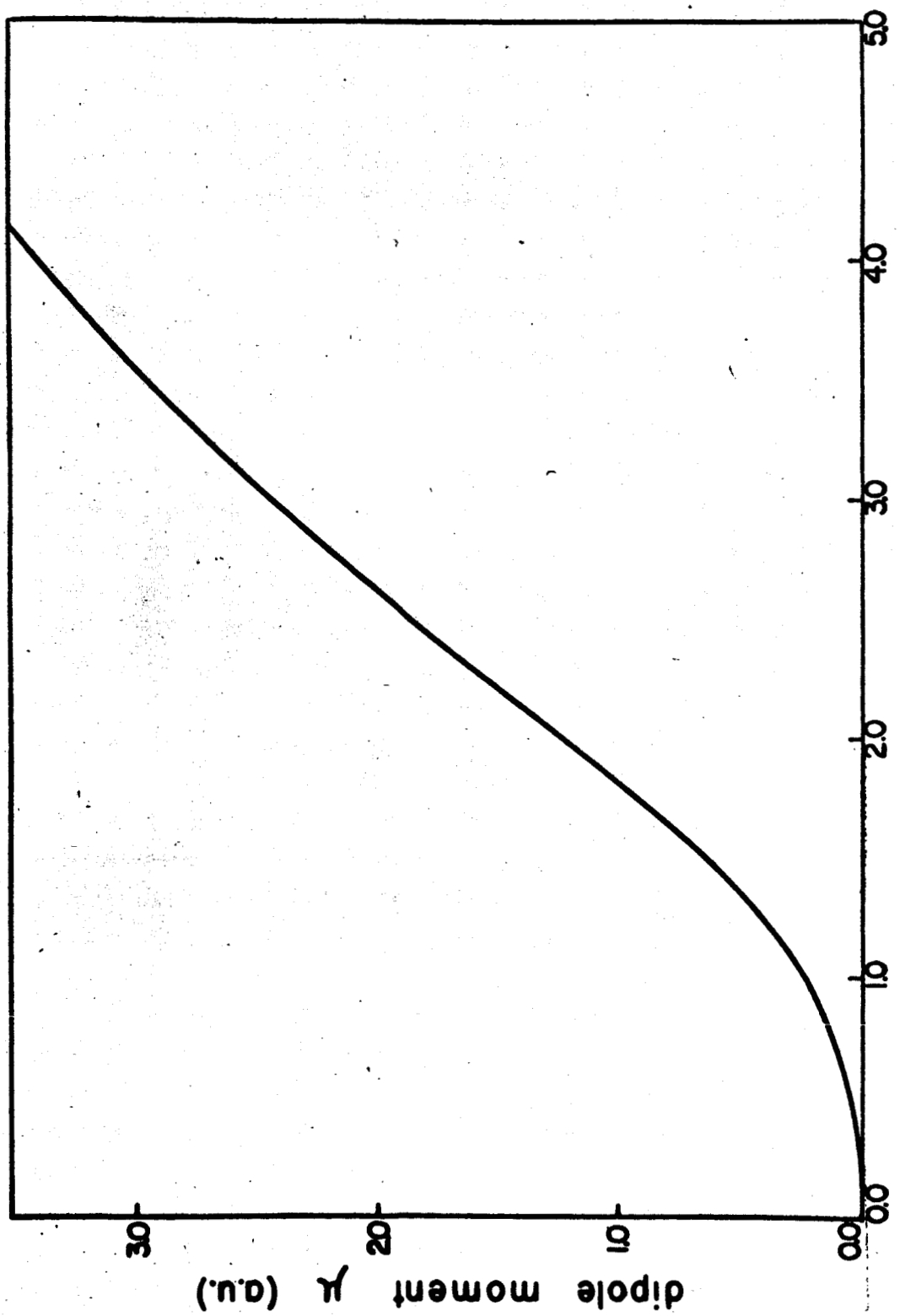

Figure 3. Dipole moment (a.u.) as function of $s = RZ_0$ for $\lambda = 1/7$, $Z_0 = 1/2$.